

PCT

THE WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁶ : C07F 7/18 (11) International Publication Number: WO 98/52954
A1 (43) International Publication Date: 26 November 1998 (26.11.98)

(21) International Application Number: PCT/CA98/00500

(22) International Filing Date: 21 May 1998 (21.05.98)

(30) Priority Data: 2,205,790 22 May 1997 (22.05.97) CA

(71) **Applicant** (*for all designated States except US*): BAYER INC.
[CA/CA]; 1265 Vidal Street South, P.O. Box 3001, Sarnia,
Ontario N7T 7M2 (CA).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): KOSKI, Ahti [CA/CA];
1876 Brigden Road, R.R. #1, Wilkesport, Ontario N0P 2R0
(CA).

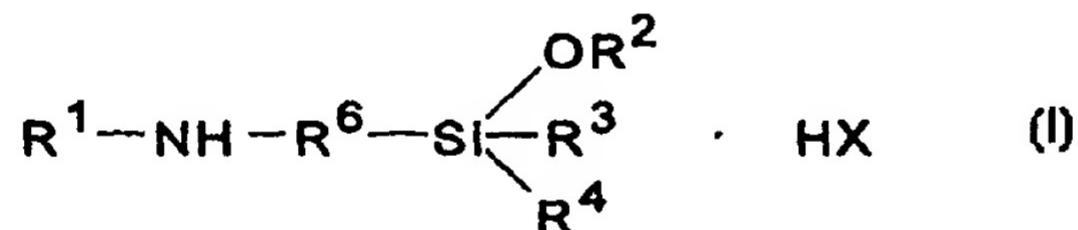
(74) Agents: NASSIF, Omar, A. et al.; Gowling, Strathy & Henderson, Suite 4900, Commerce Court West, Toronto, Ontario M5L 1J3 (CA).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: N-SUBSTITUTED-OMEGA-(ALKOXYSILYL)ALKYLAMINES AND PROCESS FOR PRODUCTION THEREOF



(57) Abstract

N-substituted- ω -(alkoxysilanes) of formula (I) wherein: R¹ is a C₁₂-C₃₀ alkyl or alkenyl group that is straight-chained or branched, a C₅-C₄₀ aryl group, a C₅-C₄₀ aralkyl group or a group R₅A(CH₂)_p wherein R₅ is a C₆-C₃₀ alkyl or alkenyl group that is straight-chained or branched, p is an integer from 2 to 6 and A is O or NH; R² is a C₁-C₁₂ alkyl group (preferably a C₁-C₅ alkyl group) or a C₃-C₁₂ alkenyl group (preferably a C₃-C₅ alkenyl group); R³ is a C₁-C₁₂ alkyl group (preferably a C₁-C₅ alkyl group), a C₁-C₁₂ alkoxy group (preferably a C₁-C₅ alkoxy group), a C₂-C₁₂ alkenyl group (preferably a C₂-C₅ alkenyl group) or a C₃-C₁₂ alkenyloxy group (preferably a C₃-C₅ alkenyloxy group); R⁴ has the same definition as R³ and may be the same as R⁴ or different; R⁶ is a divalent alkylene group having up to 10 carbon atoms and is optionally interrupted one, two or three times by a phenylene group; and X is an anion; and its free base are disclosed, and processes for their preparation. These compounds are useful for treatment of mineral particles, to alter the surface properties of the particles.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		

N-SUBSTITUTED-.OMEGA-(ALKOXYSILYL)ALKYLAMINES AND PROCESS FOR PRODUCTION THEREOF

TECHNICAL FIELD

5 The present invention relates to N-substituted- ω -(alkoxysilyl)alkylamines and salts thereof, and to a process for production thereof.

BACKGROUND ART

10 Certain silane compounds, including some amine-containing silane compounds, are said to be useful for attaching organic groups to mineral fillers; see "Silane treatment of mineral fillers - practical aspects", by E.J. Sadler, Plastics, Rubber and Composites Processing and Applications Vol. 24, No. 5, 1995, pages 271 to 275.

15 It is known to prepare some N-substituted-3-(trialkoxysilyl)-propylamines by reacting a 3-chloropropyltrialkoxysilane with a primary amine or reacting an alkyl chloride with a 3-aminopropyltrialkoxysilane, at reflux in an alcoholic solution, where the alcohol solvent corresponds to the alkyl group of the alkoxy portion of the silane. This is largely unsatisfactory as the
20 alcohols CH₃OH, C₂H₅OH and C₃H₇OH boil at temperatures below 98°C, which is lower than the temperature required to obtain good yields of the desired products in a reasonable time. While higher boiling alcohols, for example butanol, may be used to achieve higher reflux temperatures and hence increased reaction rates, this can result in an exchange of alkoxy
25 groups of the alcohol with those of the silane and a much decreased yield of the desired product. The reaction rates can be increased by using higher temperatures and a pressure autoclave, but this still requires removal of the solvent alcohol, which complicates the synthesis, and also requires specialized equipment (autoclave), which is undesirable.

30 It is also known to prepare some N-substituted-3(trialkoxysilyl)-propylamines by reacting 3-bromopropyltrialkoxysilane with a primary amine, or reacting an alkyl bromide with a 3-aminopropyltrialkoxysilane at reflux in alcohol solution. Again, it is desirable that the alkoxy group of the alcohol is the same as the alkoxy group of the silane. While in some cases satisfactory

- 2 -

yields can be obtained, in others the temperature of the boiling solvent is too high, causing unwanted side reactions, for instance dehydrobromination of the starting 3-bromopropyltrialkoxysilane. In any case, it is necessary to remove the alcohol to obtain the required product, which is expensive and
 5 disadvantageous, particularly if it is important to remove all traces of the solvents.

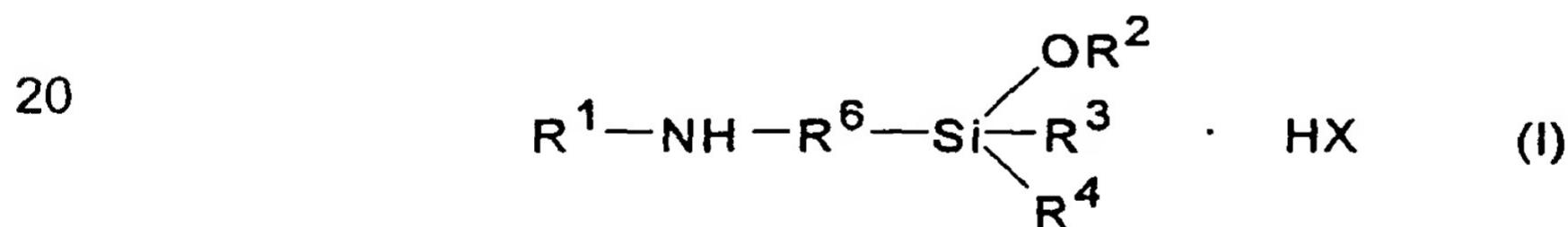
SUMMARY OF THE INVENTION

It is an object of the present invention to obviate or mitigate at
 10 least one of the above-identified disadvantages of the prior art.

It is another object of the present invention to provide novel N-substituted- ω -(alkoxysilyl)alkylamines and salts thereof.

It is yet another object of the present invention to provide a novel process for producing N-substituted- ω -(alkoxysilyl)alkylamines and salts
 15 thereof.

Accordingly, in one of its aspects, the present invention provides a process for producing a compound of Formula I:



wherein R¹ is a C₆-C₄₀ alkyl or alkenyl group that is straight-chained or
 25 branched, a C₆-C₄₀ aryl group, a C₇-C₄₀ aralkyl group or a group R₅A(CH₂)_p,
 wherein R₅ is a C₆-C₃₀ alkyl or alkenyl group that is straight-chained or
 branched, p is an integer from 2 to 6 and A is O or NH;

R² is a C₁-C₁₂ alkyl group (preferably a C₁-C₅ alkyl group) or a
 C₃-C₁₂ alkenyl group (preferably a C₃-C₅ alkenyl group);

- 30 R³ is a C₁-C₁₂ alkyl group (preferably a C₁-C₅ alkyl group), a C₁-C₁₂ alkoxy group (preferably a C₁-C₅ alkoxy group), a C₂-C₁₂ alkenyl group (preferably a C₂-C₅ alkenyl group) or a C₃-C₁₂ alkenyloxy group (preferably a

- 3 -

C_3 - C_5 alkenyloxy group);

R^4 has the same definition as R^3 and may be the same as R^4 or different;

R^6 is a divalent alkylene group having up to 10 carbon atoms

5 and is optionally interrupted one, two or three times by a phenylene group; and

X is an anion;

the process comprising the step of:

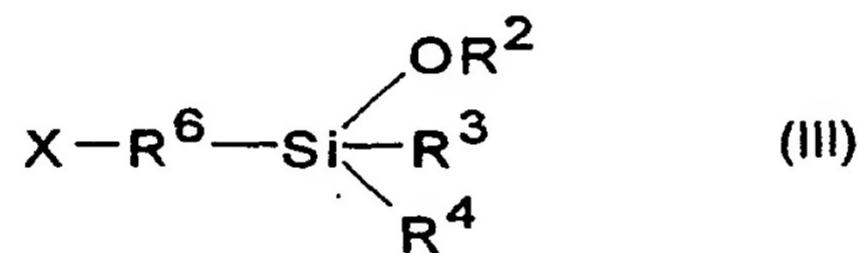
(a) reacting a compound of the Formula II:

10



wherein R^1 is as defined above, with a compound of Formula III:

15



20 wherein R^2 , R^3 , R^4 , R^6 and X are as defined above, in the absence of a solvent; or

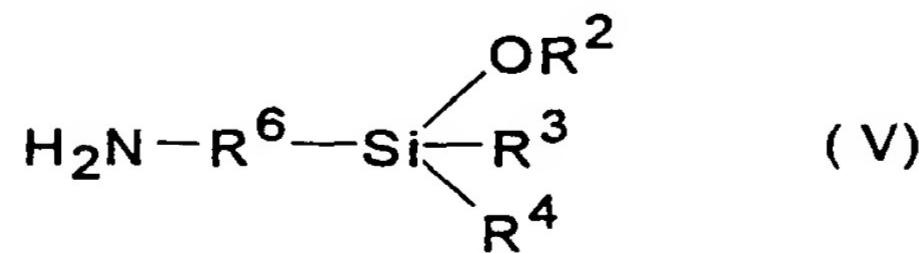
(b) reacting a compound of the Formula IV:



25

wherein R^1 and X are as defined above, with a compound of Formula V:

30

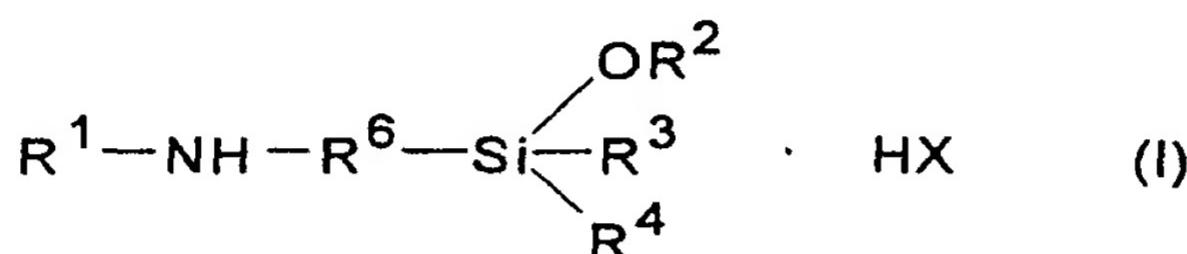


- 4 -

wherein R², R³, R⁴ and R⁶ are as defined above, in the absence of a solvent.

It is surprising that the N-substituted- ω -(alkoxysilyl)alkylamines of Formula I can be obtained in good yields, within reasonable reaction times, without contamination by alcoholic solvent and without necessity for removal
5 of alcoholic solvent.

In another of its aspects, the present invention provides a compound of Formula I:



wherein R¹ is a C₁₂-C₄₀ alkyl or alkenyl group that is straight-chained or
15 branched, a C₆-C₄₀ aryl group, a C₇-C₄₀ aralkyl group or a group R₅A(CH₂)_p
wherein R₅ is a C₆-C₃₀ alkyl or alkenyl group that is straight-chained or
branched, p is an integer from 2 to 6 and A is O or NH;

R² is a C₁-C₁₂ alkyl group (preferably a C₁-C₅ alkyl group) or a C₃-C₁₂ alkenyl group (preferably a C₃-C₅ alkenyl group);

20 R³ is a C₁-C₁₂ alkyl group (preferably a C₁-C₅ alkyl group), a C₁-C₁₂ alkoxy group (preferably a C₁-C₅ alkoxy group), a C₂-C₁₂ alkenyl group (preferably a C₂-C₅ alkenyl group) or a C₃-C₁₂ alkenyloxy group (preferably a C₃-C₅ alkenyloxy group);

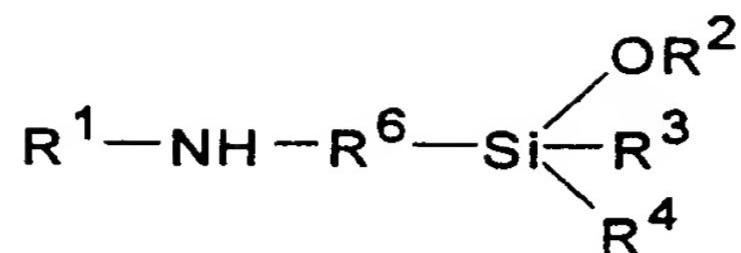
25 R⁴ has the same definition as R³ and may be the same as R⁴ or different;

R⁶ is a divalent alkylene group having up to 10 carbon atoms and is optionally interrupted one, two or three times by a phenylene group; and

X is an anion.

30 In another of its aspects, the present invention provides a compound of Formula I:

- 5 -



5

wherein R¹ is a C₁₂-C₄₀ alkyl or alkenyl group that is straight-chained or branched, a C₆-C₄₀ aryl group, a C₇-C₄₀ aralkyl group or a group R₅A(CH₂)_p,

wherein R₅ is a C₆-C₃₀ alkyl or alkenyl group that is straight-chained or

10 branched, p is an integer from 2 to 6 and A is O or NH;

R² is a C₁-C₁₂ alkyl group (preferably a C₁-C₅ alkyl group) or a C₃-C₁₂ alkenyl group (preferably a C₃-C₅ alkenyl group);

R³ is a C₁-C₁₂ alkyl group (preferably a C₁-C₅ alkyl group), a C₁-C₁₂ alkoxy group (preferably a C₁-C₅ alkoxy group), a C₂-C₁₂ alkenyl group

15 (preferably a C₂-C₅ alkenyl group) or a C₃-C₁₂ alkenyloxy group (preferably a C₃-C₅ alkenyloxy group);

R⁴ has the same definition as R³ and may be the same as R⁴ or different; and

R⁶ is a divalent alkylene group having up to 10 carbon atoms

20 and is optionally interrupted one, two or three times by a phenylene group.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The anion X is suitably a chloride, bromide or iodide anion, of which the chloride and the bromide are preferred. The preferred reaction

25 conditions vary, depending upon whether X is chlorine or bromine. If X is chlorine, it is preferred to carry out the reaction at a temperature at least about 100°C, more preferably in the range of from about 130°C to about 185°C. The reaction may take anywhere from about 30 minutes to about 4 hours. If X is bromine, then it is preferred to operate at a lower temperature, preferably from about 30°C to about 75°C. With bromine the reaction proceeds more slowly and reaction times of from about 8 to 24 hours are not unusual.

- 6 -

In one embodiment of the present process, an amine compound of Formula II is reacted with an alkoxy silane compound of Formula III.

Non-limiting examples of suitable amines of Formula II may be selected from the group comprising hexylamine, octylamine, nonylamine, decylamine, octadecylamine, octadec-9-enylamine and mixtures thereof.

Indeed, mixed amines are commercially available and these are conveniently suitable for use. Non-limited examples of such amines may be selected from the group comprising soya amine, tall oil amine, stearyl amine, tallow amine, dihydrogenated tallow amine, cocoamine, rosin amine, palmitylamine and mixtures thereof. These amines may be used in distilled or undistilled form. When R¹ is alkenyl, it may contain one, two or more double bonds and when it contains two or more double bonds, they may be conjugated or unconjugated.

In another embodiment of the present process, an amine compound of Formula IV is reacted with an alkoxy silane compound of Formula V.

Non-limiting examples of suitable alkyl or alkenyl halides of Formula IV may be selected from the group comprising 1-bromo octane, 1-chlorononane, 1-bromononane, 1-bromodecane, 1-chlorododecane, 1-bromo octadecane, 1-bromo octadec-9-ene and mixtures thereof. Indeed, mixed alkyl/alkenyl halides are commercially available and these are conveniently suitable for use. Non-limited examples of such alkyl/alkenyl halides may be selected from the stearyl chloride, stearyl bromide, oleyl chloride and mixtures thereof. These materials may be used in distilled or undistilled form. Again, R¹ is alkenyl, it may contain one, two or more double bonds and when it contains two or more double bonds, they may be conjugated or unconjugated.

In the compound of Formula III or V, as stated R² is preferably C₁-C₅ alkyl or C₃-C₅ alkenyl, but more preferably it is C₁-C₃ alkyl, i.e., methyl, ethyl, propyl or isopropyl. It is preferred that R³ and R⁴ are C₁-C₅ alkoxy, particularly methoxy, ethoxy, propoxy or isopropoxy. It is preferred that OR², R³ and R⁴ are all the same and are methoxy. If OR², R³ and R⁴ are not the

- 7 -

same it is preferred that R³ and R⁴ are alkyl or alkenyl. Preferably R², R³ and R⁴ are unsubstituted, but the use of substituted groups is not excluded, provided that the substituent does not interfere with the course of the reaction. These remarks also apply in respect of R¹ and R⁶.

5 The reactions may be carried out under inert atmosphere, for example by flushing the reactor with an inert gas such as argon or nitrogen. This is not essential, however.

The reaction of the compound of Formula II with the compound of Formula III, or the compound of Formula IV with the compound of Formula 10 V, results in release of the acid HX. Generally, the product of reaction will therefore be in the form of its acid addition salt with HX. For many purposes the compounds of Formula I can be used in the form of their salts.

Alternatively, they can be converted from the salt to the free base, if needed. This is best done by reacting the compound with an alkali metal alkoxide in 15 which the alkyl moiety is R², as defined above. For instance, if R² is methyl, it is preferred to use sodium methoxide to convert the salt to the free base.

Particularly, if the compounds of Formula I are to be used to render a material hydrophobic, it is preferred that R¹ is a longer chain alkyl or alkenyl group that preferably has ten carbon atoms, more preferably twelve 20 carbon atoms, and more, and it is preferred that the chain is not branched at the atom connecting R¹ to the nitrogen.

It is believed that compounds of Formula I, prepared from mixed amines of more than 12 carbon atoms are novel. Thus, these compounds, in the acid addition salt form or free base form, are another aspect of the 25 invention.

The compounds of Formula I are useful for treating mineral fillers to alter the properties of the mineral fillers. They can be used, for example, to treat silica, silicate mineral powders, clays, calcium carbonate, pigments such as titanium dioxide and other materials to render their surfaces 30 hydrophobic. They can also be used as intermediates in the preparation of silica-bound catalysts and intermediates or ion-exchangers, or as coupling agents to improve the bond between paint and a wood or metal substrate, or

as a waterproofing agent for wood or concrete.

Embodiments of the invention will be illustrated with reference to the following Examples which should to be used to construe or limit the scope of the invention.

5

Example 1 - Oleyl amine:(3-chloropropyl)trimethoxysilane 1:1 Adduct N-Oleyl-N-(3-trimethoxysilyl)propylamine (R¹ = oleyl)

To a 1000 ml Erlenmeyer flask were added 267.5 grams of distilled oleylamine (Witco Kemamine 989D) and 198.8 grams of (3-chloropropyl)trimethoxysilane (Aldrich). A magnetic stirring bar and thermometer were inserted and the headspace above the liquid was flushed with Argon gas. The neck of the flask was then loosely plugged with tissue to hold the thermometer in place. The flask was placed on a hot plate and slowly heated to 160°C over a period of 90 minutes with stirring. On cooling, the title compound, in the form of a yellow waxy solid (464.2 grams, m.p. 68-74°C) was obtained. The material was readily soluble in methanol.

Example 2 - Palmityl amine:(3-chloropropyl)trimethoxysilane 1:1 Adduct N-Palmityl-N-(3-trimethoxysilyl)propylamine (R = palmityl)

20 To a 250 ml Erlenmeyer flask were added 60.5 grams of distilled palmitylamine (Akzo-Nobel Armeen 16D) and 50.4 grams of (3-chloropropyl)trimethoxysilane (Aldrich). A magnetic stirring bar and thermometer were inserted and the headspace above the slurry was flushed with Argon gas. The neck of the flask was then loosely plugged with tissue to hold the thermometer in place. The flask was placed on a hot plate and slowly heated with stirring to 50°C to dissolve the amine. The heat was then increased and the contents were heated to 170°C over a period of 30 minutes with stirring and then held at that temperature for 10 minutes. The heat was turned off and the flask was allowed to cool to room temperature over a one hour period. At 110°C, a yellow solid began to separate. The final yield was 30 107.1 grams of the title compound in the form of a yellow waxy solid (m.p. 106-110°C) which dissolved readily in methanol.

- 9 -

Example 3 - Stearylamine:(3-chloropropyl)trimethoxysilane 1:1 Adduct

N-Stearyl-N-(3-trimethoxysilyl)propylamine (R¹ = stearyl)

To a 250 ml Erlenmeyer flask were added 76.7 grams of distilled stearylamine (Akzo-Nobel Armeen 18D) and 57.4 grams of (3-chloropropyl)trimethoxysilane (Aldrich). A magnetic stirring bar and thermometer were inserted. The neck of the flask was loosely plugged with tissue to hold the thermometer in place. The flask was placed on a hot plate and heated rapidly with stirring to 198°C at which point the heat was shut off. The reaction exothermicity kept the temperature at 190°C for 10 minutes after which the material cooled quickly to room temperature. At 130°C, a yellow solid began to separate. The final yield was 131.4 grams of the title compound in the form of a yellow waxy solid (m.p. 120-135°C), easily soluble in methanol.

15 Example 4 - Dodecyl amine:(3-chloropropyl)trimethoxysilane 1:1 Adduct

N-Dodecyl-N-(3-trimethoxysilyl)propylamine (R¹ = dodecyl)

To a 250 ml Erlenmeyer flask were added 22.9 grams of dodecylamine (Aldrich) and 24.8 grams of (3-chloropropyl)trimethoxysilane (Aldrich). A magnetic stirring bar and thermometer were inserted. The neck of the flask was then loosely plugged with tissue to hold the thermometer in place. The flask was placed on a hot plate and heated slowly to 185°C with stirring, at which point the heat was reduced and the contents kept at 175-180°C for 20 minutes. The heat was then shut off and the flask contents were allowed to cool. Solidification of the contents to an off-white solid began at around 50°C. The final product (47.3 grams) dissolved quickly in methanol with gentle stirring.

Example 5 - C-18 Tertiary alkyl primary amine:(3-chloropropyl)tri-

methoxysilane 1:1 Adduct (R¹ = C-18 tertiary primary alkyl)

30 To a 1000 ml Erlenmeyer flask were added 162.5 grams of C-18 tertiary alkyl primary amine (Primene JM-T, Rohm and Haas) and 100.4 grams of (3-chloropropyl)trimethoxysilane (Aldrich). A magnetic stirring bar

- 10 -

and thermometer were inserted. The neck of the flask was then loosely plugged with tissue to hold the thermometer in place. The flask was placed on a hot plate and heated slowly over a period of 95 minutes to 180°C with stirring, at which point the heat was shut off and the flask contents were

5 allowed to cool. No solidification occurred. 258.9 grams of a viscous amber liquid were recovered. The liquid was miscible with methanol in all proportions.

Example 6 - Tallow amine:(3-chloropropyl)trimethoxysilane 1:1 Adduct N-

10 Tallow-alkyl-N-(3-trimethoxysilyl)propylamine (R¹ = tallow alkyl)

To a 1000 ml Erlenmeyer flask were added 134 grams of distilled tallow amine (Armeen TD, Akzo-Nobel) and 100.4 grams of (3-chloropropyl)trimethoxysilane (Aldrich). A magnetic stirring bar and thermometer were inserted. The neck of the flask was then loosely plugged with tissue to hold the thermometer in place, a needle was inserted and the headspace was flushed with Argon to remove air. The flask was placed on a hot plate and heated over a period of one hour to 180°C with stirring, at which point the heat was shut off. The heat of reaction continued to raise the temperature to 192°C after which the material cooled to room temperature over one hour. Solidification of the contents began at 65°C and the material was completely solid by 55°C. The yield was 234 grams of a yellowish pasty solid. This material dissolved easily in methanol to give a clear solution.

Example 7 - Octyl amine:(3-chloropropyl)trimethoxysilane 1:1 Adduct

25 N-Octyl-N-(3-trimethoxysilyl)propylamine (R¹ = octyl)

To a 500 ml 2-neck round bottom flask equipped with a drying tube and magnetic stirrer were added 99.5 grams of octylamine (Aldrich) and 154.5 grams of (3-chloropropyl)trimethoxysilane (Aldrich). A thermometer was inserted through a side arm. The flask was placed in a mantle equipped with a Variac controller and the heat was energized. Over a period of 85 minutes, the temperature climbed to 190°C and then fell to 180°C within 25 minutes at which point the heat was shut off. Solidification of

- 11 -

the contents began at 60°C and the material was completely solid by 50°C. The yield was 253.6 grams of the title compound in the form of a yellow solid. This material dissolved readily in methanol to give a clear yellow solution.

5 Example 8 - Cocoamine:(3-chloropropyl)trimethoxysilane 1:1 Adduct (R¹ = cocoa alkyl)

To a 500 ml Erlenmeyer flask were added 100 grams of distilled cocoamine (Armeen CD, Akzo-Nobel) and 100 grams of (3-chloropropyl)-trimethoxysilane (Aldrich). A magnetic stirring bar and thermometer were 10 inserted and the neck of the flask was then loosely plugged with tissue to hold the thermometer in place. The flask was placed on a hot plate and heated over a period of 45 minutes to 185°C with stirring, at which point the heat was turned off. The heat of reaction continued to raise the temperature to 200°C 15 over 5 minutes after which it fell to 125°C 20 minutes later. 198.4 grams of product were isolated. At room temperature, the material was a yellow waxy 15 solid which dissolved easily in methanol on gentle shaking.

Example 9 - 1-Chlorodecane:(3-aminopropyl)trimethoxysilane 1:1 Adduct N-Decyl-N-(3-trimethoxysilyl)propylamine (R¹ = decyl)

20 To a 500 ml Erlenmeyer flask were added 95 grams of 1-chlorodecane (Aldrich) and 96.4 grams of (3-aminopropyl)trimethoxysilane (Petrarch/UCT). A magnetic stirring bar and thermometer were inserted and the neck of the flask was then loosely plugged with tissue to hold the thermometer in place. The flask was placed on a hot plate and heated with 25 stirring. After 90 minutes the temperature reached 184°C and then fell to 175°C 20 minutes later at which point the heat was turned off and the material removed from the hot plate. When cooled, the material was a waxy solid, and was recovered which dissolved easily in methanol.

30 Example 10- 1-Bromododecane:(3-aminopropyl)trimethoxysilane 1:1 Adduct N-Dodecyl-N-(3-trimethoxysilyl)propylamine (R¹ = dodecyl)

To a 100 ml Erlenmeyer flask were added 24.9 grams of 1-

- 12 -

bromododecane (Aldrich) and 17.9 grams of (3-aminopropyl)trimethoxysilane (Petrarch/UCT). The flask was stoppered and shaken to effect mixing. The material was allowed to stand undisturbed at room temperature (23°C) for 5 hours. Examination of the mixture after this period revealed an upper phase 5 consisting of a clear liquid and a lower phase of feathery white crystals. The flask was transferred to a hot plate previously equilibrated to give a surface temperature of 45° and left for 16 hours. At the end of this time all the material had reacted to give 41.2 grams of pale yellow crystals. An NMR spectrum was consistent with that expected from N-dodecyl-N-(3- 10 trimethoxysilyl)propyl ammonium bromide. The material was freely soluble in methanol with a distinct endothermic effect.

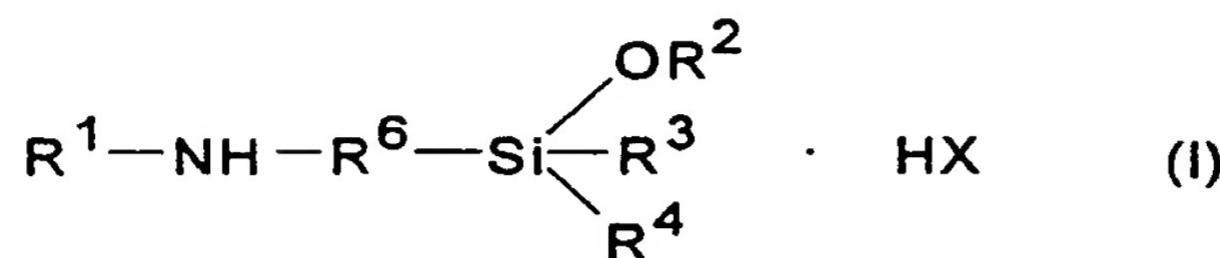
Example 11- Soya amine:(3-chloropropyl)trimethoxysilane 1:1 Adduct (R¹ = soya-alkyl)

15 To a 1000 ml Erlenmeyer flask were added 263.6 grams of distilled soya amine (Akzo-Nobel Armeen SD) and 198.7 grams of (3-chloropropyl)trimethoxysilane (Aldrich). A magnetic stirring bar and thermometer were inserted. The neck of the flask was loosely plugged with tissue to hold the thermometer in place. The flask was placed on a hot plate 20 and heated slowly to 45° in order to effect solution of the soya amine. It was then heated to 160°C over two hours and then held at 147-160°C for a further two hours after which it was allowed to cool slowly to room temperature. Yellow crystals began to separate from the mother liquid at 75°C and at room temperature the contents of the flask comprised a yellow solid mass. 25 The yield was 460.0 grams. The product was easily soluble in methanol to give a clear yellowish solution.

- 13 -

What is claimed is:

1. A process for producing a compound of Formula I:



wherein R¹ is a C₆-C₄₀ alkyl or alkenyl group that is straight-chained or branched, a C₆-C₄₀ aryl group, a C₇-C₄₀ aralkyl group or a group R₅A(CH₂)_p wherein R₅ is a C₆-C₃₀ alkyl or alkenyl group that is straight-chained or branched, p is an integer from 2 to 6 and A is O or NH;

R² is a C₁-C₁₂ alkyl group or a C₃-C₁₂ alkenyl group;

R³ is a C₁-C₁₂ alkyl group, a C₁-C₁₂ alkoxy group, a C₂-C₁₂ alkenyl group or a C₃-C₁₂ alkenyloxy group;

R⁴ has the same definition as R³ and may be the same as R⁴ or different;

R⁶ is a divalent alkylene group having up to 10 carbon atoms and is optionally interrupted one, two or three times by a phenylene group; and

X is an anion;

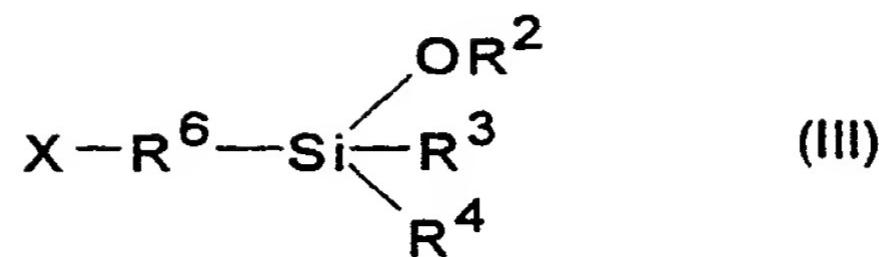
the process comprising the step of:

- (a) reacting a compound of the Formula II:



wherein R¹ is as defined above, with a compound of Formula III:

- 14 -

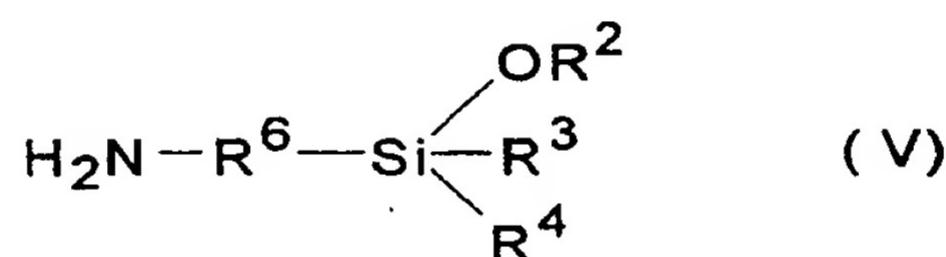


wherein R², R³, R⁴, R⁶ and X are as defined above, in the absence of a solvent; or

(b) reacting a compound of the Formula IV:



wherein R¹ and X are as defined above with a compound of Formula V:



wherein R², R³, R⁴ and R⁶ are as defined above, in the absence of a solvent.

2. The process defined in claim 1, wherein, R² is a C₁-C₅ alkyl group.
 3. The process defined in claim 1, wherein R² is a C₃-C₅ alkenyl group.
 4. The process defined in any one of claims 1-3, wherein R³ is a C₁-C₅ alkyl group.
 5. The process defined in any one of claims 1-3, wherein R³ is a C₁-C₅ alkoxy group.

- 15 -

6. The process defined in any one of claims 1-3, wherein R³ is a C₂-C₅ alkenyl group.
7. The process defined in any one of claims 1-3, wherein R³ is a C₃-C₅ alkenyloxy group.
8. The process defined in any one of claims 1-7, wherein X is chlorine.
9. The process defined in claim 8, wherein the reactants are heated to a temperature of at least about 100°C.
10. The process defined in claim 8, wherein the reactants are heated to a temperature in the range from about 130° to about 185°C.
11. The process defined in any one of claims 1-7, wherein X is bromine.
12. The process defined in claim 11, wherein the reactants are heated to temperature in the range from about 30° to about 50°C.
13. The process defined in any one of claims 1-12, wherein R⁶ is the group -(CH₂)₃-.
14. The process defined in any one of claims 1-13, wherein R² is a C₁-C₃ alkyl group and R³ and R⁴ are each a C₁-C₃ alkoxy group.
15. The process defined in any one of claims 1-13, wherein R² is methyl and R³ and R⁴ are each a methoxy group.
16. The process defined in any one of claims 1-15, wherein R⁶ is

- 16 -

the group $-(\text{CH}_2)_3-$, R^2 is methyl and R^3 and R^4 are each a methoxy group.

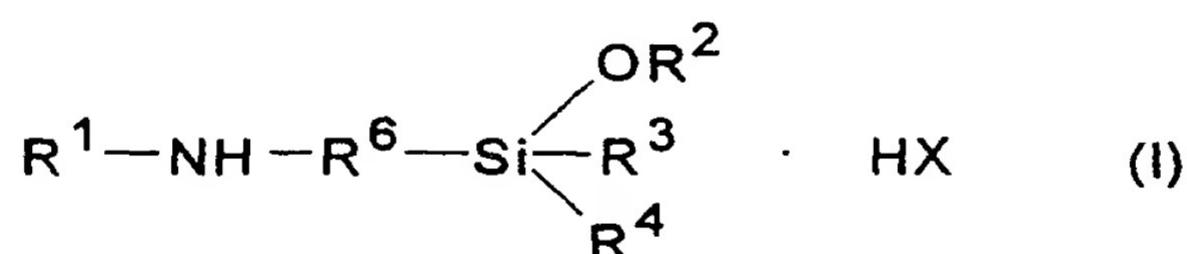
17. The process defined in any one of claims 1-16, wherein the compound of Formula II is oleylamine.

18. The process defined in any one of claims 1-16, wherein the compound of Formula II is soya-amine.

19. The process defined in any one of claims 1-16, wherein the compound of Formula II is tall-oil-amine.

20. The process defined in any one of claims 1-19, wherein the compound of Formula III is (3-chloropropyl)trimethoxysilane.

21. A compound of Formula I:



wherein R^1 is a C_{12} - C_{40} alkyl or alkenyl group that is straight-chained or branched, a C_6 - C_{40} aryl group, a C_7 - C_{40} aralkyl group or a group $\text{R}_5\text{A}(\text{CH}_2)_p$ wherein R_5 is a C_6 - C_{30} alkyl or alkenyl group that is straight-chained or branched, p is an integer from 2 to 6 and A is O or NH;

R^2 is a C_1 - C_{12} alkyl group or a C_3 - C_{12} alkenyl group;

R^3 is a C_1 - C_{12} alkyl group, a C_1 - C_{12} alkoxy group, a C_2 - C_{12} alkenyl group or a C_3 - C_{12} alkenyloxy group;

R^4 has the same definition as R^3 and may be the same as R^2 or different;

R^6 is a divalent alkylene group having up to 10 carbon atoms and is optionally interrupted one, two or three times by a phenylene group;

- 17 -

and

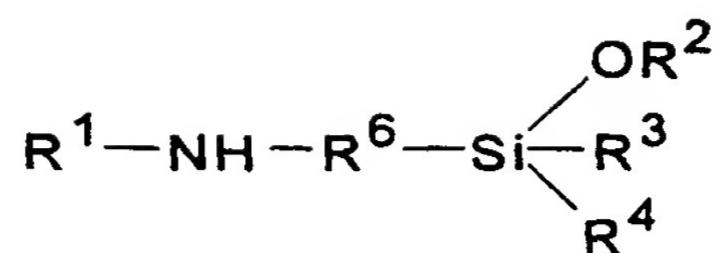
X is an anion.

22. The compound defined in claim 21, wherein, R² is a C₁-C₅ alkyl group.
23. The compound defined in claim 21, wherein R² is a C₃-C₅ alkenyl group.
24. The compound defined in any one of claims 21-23, wherein R³ is a C₁-C₅ alkyl group.
25. The compound defined in any one of claims 21-23, wherein R³ is a C₁-C₅ alkoxy group.
26. The compound defined in any one of claims 21-23, wherein R³ is a C₂-C₅ alkenyl group.
27. The compound defined in any one of claims 21-23, wherein R³ is a C₃-C₅ alkenyloxy group.
28. The compound defined in claim 21, wherein R⁶ is the group -(CH₂)₃-, R² is methyl and R³ and R⁴ are each a methoxy group.
29. The compound defined in claim 21, wherein R¹ is soya-alkyl, R⁶ is the group -(CH₂)₃-, R² is methyl and R³ and R⁴ are each a methoxy group, and salts thereof.
30. The compound defined in claim 21, wherein R¹ is tall-oil-alkyl, R⁶ is the group -(CH₂)₃-, R² is methyl and R³ and R⁴ are each a methoxy group, and salts thereof.

- 18 -

31. The compound defined in any one of claims 21-30, as the hydrochloride salt.
32. *N*-oleyl-*N*-(3-trimethoxysilyl)propyl amine, and salts thereof.
33. *N*-oleyl-*N*-(3-trimethoxysilyl)propyl ammonium chloride.
34. Use of a compound prepared by the process defined in any one of claims 1-20 for hydrophobicizing particles for use as filler in a polymer masterbatch.
35. Use of a compound prepared by the process defined in any one of claims 1-20 for hydrophobicizing particles for use as filler in a rubber vulcanizate.
36. Use of a compound defined in any one of claims 21-33 for hydrophobicizing particles for use as filler in a rubber vulcanizate.
37. Use of a compound defined in any one of claims 21-33 for hydrophobicizing particles for use as filler in a polymer masterbatch.
38. Use according to any one of claims 34-37, wherein the particles are hydrophilic mineral particles that have surface hydroxyl groups.
39. Use according to claim 38, wherein the particles are selected from silica, silicates, clay, alumina and titanium dioxide.
40. A compound of Formula:

- 19 -



wherein R¹ is a C₁₂-C₄₀ alkyl or alkenyl group that is straight-chained or branched, a C₆-C₄₀ aryl group, a C₇-C₄₀ aralkyl group or a group R₅A(CH₂)_p, wherein R₅ is a C₆-C₃₀ alkyl or alkenyl group that is straight-chained or branched, p is an integer from 2 to 6 and A is O or NH;

R² is a C₁-C₁₂ alkyl group or a C₃-C₁₂ alkenyl group;

R³ is a C₁-C₁₂ alkyl group, a C₁-C₁₂ alkoxy group, a C₂-C₁₂ alkenyl group or a C₃-C₁₂ alkenyloxy group;

R⁴ has the same definition as R³ and may be the same as R⁴ or different; and

R⁶ is a divalent alkylene group having up to 10 carbon atoms and is optionally interrupted one, two or three times by a phenylene group.

41. The compound defined in claim 40, wherein, R² is a C₁-C₅ alkyl group.
42. The compound defined in claim 40, wherein R² is a C₃-C₅ alkenyl group.
43. The compound defined in any one of claims 40-42, wherein R³ is a C₁-C₅ alkyl group.
44. The compound defined in any one of claims 40-42, wherein R³ is a C₁-C₅ alkoxy group.
45. The compound defined in any one of claims 40-42, wherein R³ is a C₂-C₅ alkenyl group.

- 20 -

46. The compound defined in any one of claims 40-42, wherein R³ is a C₃-C₅ alkenyloxy group.
47. The compound defined in claim 40, wherein R⁶ is -(CH₂)₃-, R² is methyl and R³ and R⁴ are each a methoxy group.
48. The compound defined in claim 40, wherein R¹ is soya-alkyl, R⁶ is -(CH₂)₃-, R² is methyl and R³ and R⁴ are each a methoxy group, and salts thereof.
49. The compound defined in claim 40, wherein R¹ is tall-oil-alkyl, R⁶ is -(CH₂)₃-, R² is methyl and R³ and R⁴ are each a methoxy group, and salts thereof.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 98/00500

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07F7/18

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>CHEMICAL ABSTRACTS, vol. 117, no. 24, 14 December 1992 Columbus, Ohio, US; abstract no. 244151, YAMAGUCHI, TAKAHIRO ET AL: "Laminated sheet for electrical insulation and its manufacture" XP002071248 see abstract & JP 04 208 459 A (SHIN-KOBE ELECTRIC MACHINERY CO., LTD., JAPAN) ----</p> <p style="text-align: center;">-/--</p>	21-49

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

13 July 1998

Date of mailing of the international search report

31/07/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Rinkel, L

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 98/00500

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 126, no. 13, 25 March 1997 Columbus, Ohio, US; abstract no. 172736, SUZUKI, YOSHIHARU: "Silane coupling agents for glass fibers and manufacture of glass fiber-reinforced epoxy resin moldings with improved solder-heat resistance" XP002071249 see abstract & JP 08 325 439 A (NITTO BOSEKI CO LTD, JAPAN) ---	21-49
X	CHEMICAL ABSTRACTS, vol. 104, no. 22, 2 June 1986 Columbus, Ohio, US; abstract no. 196864, KUWAHARA, MICHIO ET AL: "Measurement of surface coupling coefficients between nematic liquid crystals and various substrates" XP002071250 see abstract & DENSHI TSUSHIN GAKKAI RONBUNSHI, C (1985), J68-C(10), 825-33 CODEN: DTGCAY, ---	21-49
X	DE 19 55 023 A (DOW CORNING CORPORATION) 14 May 1970 see the whole document ---	21-49
A	DE 26 48 240 A (DOW CORNING CORPORATION) 30 June 1977 see the whole document ---	1-20
A	EP 0 595 488 A (SHIN-ETSU CHEMICAL CO., LTD.) 4 May 1994 see the whole document -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 98/00500

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
DE 1955023	A	14-05-1970	AT	290043 A	15-03-1971
			BE	741074 A	30-04-1970
			FR	2022367 A	31-07-1970
			GB	1233854 A	03-06-1971
			NL	6916414 A	06-05-1970
			SE	339982 B	01-11-1971
			US	3560385 A	02-02-1971
DE 2648240	A	30-06-1977	US	4064155 A	20-12-1977
			CA	1076595 A	29-04-1980
			FR	2336406 A	22-07-1977
			GB	1540627 A	14-02-1979
			JP	1066515 C	30-09-1981
			JP	52078834 A	02-07-1977
			JP	56008837 B	25-02-1981
EP 595488	A	04-05-1994	JP	6135974 A	17-05-1994
			US	5446181 A	29-08-1995

